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Pollution Volatility	Pollution Control	13B 20M
Coal	Stationary Sources	21D
Combustion	Fuel Nitrogen	21B
Emission	Firing Conditions	14G
Nitrogen Oxide (NO)		07B
Nitrogen		

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JOURNAL ARTICLE

Influence of fuel composition on nitric oxide formation in mass-burning stokers

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Seven coals of varying rank were tested in an experimental mass-burning simulation to assess general nitric oxide (NO) emission characteristics. Comparisons were made among the fuels to ascertain a relationship between nitric oxide emissions, fuel nitrogen content, nitrogen volatility and firing conditions. Considerable variability in exhaust NO emissions was observed among coal types, even for coals of common rank fired under similar thermal and stoichiometric conditions. Fuel nitrogen conversion to NO was not singularly dependent on inherent nitrogen content or volatility. A correlation was developed to estimate NO emissions based on both coal nitrogen content and char nitrogen fraction for combustion conditions typical of mass-burning stokers.

(Keywords: fuel; nitrogen compounds; coal)

Investigations of nitrogen oxides (NO_x) emissions from mass-burning stoker systems have been very limited. Control schemes for nitric oxide (NO) abatement have been primarily confined to the utilization of existing equipment operated under constrained conditions. To date, NO_x emissions control has yet to be generally implemented at operating coal-fired, mass-burning stoker installations.

Pilot and large-scale testing has partially demonstrated the potential for reducing NO_x emissions through modified operating procedures[1,2]. Recent studies[3,4] have contributed to the characterization of combustion parameters affecting NO formation and reaction in thick coal-bed firing. These studies have been principally concerned with the fate of volatile nitrogenous species as influenced by the local combustion environment.

This paper describes the results of an experimental investigation of fuel composition effects on NO formation in fixed-bed combustion. The purpose of the work was to ascertain a relationship between NO emissions, fuel nitrogen content, nitrogen volatility and firing conditions. Specifically, seven coals of varying rank were fired in an experimental mass-burning furnace to assess general NO emissions characteristics. Bed-region (first stage) and overall furnace stoichiometric ratios were used in data correlation. The stoichiometric ratio was defined as the ratio of available combustion air to the air required for complete combustion to theoretical products. Exhaust emissions were measured as NO, but reported in terms of NO_x as ng NO_2/J (1b $NO_2/10^6$ Btu), in accordance with standard EPA practice.

EXPERIMENTAL

An experimental fixed-bed furnace was utilized to simulate the fuel-bed burning regime in a coal-fired mass-burning stoker[4]. The combustor was designed for firing rates comparable to commercial travelling grate stokers, 1.27 to 1.58 MW/m^2 with a total surface area of 390 cm^2. Several sampling ports and windows were available for monitoring local combustion conditions.

Primary combustion air (underfire air) was supplied through a single plenum beneath the fuel bed. Secondary combustion air (overfire air) was introduced to the over-bed region as high velocity air-jets (approximately 30.5 ms^{-1}), injected normal to the axial (vertical) flow of combustion gases to provide turbulent mixing. The combustion air was metered with rotameters and supplied at ambient temperature.

Exhaust gas samples were taken from the flue through a water-cooled stainless-steel probe. Winter[5] demonstrated that the probe design was effective in quenching combustion reactions and providing a representative sample of local species concentrations. Measurements were made continuously, and included chemiluminescence NO/NO_2, paramagnetic O_2, and NDIR CO and CO_2. Fuel-bed temperatures were monitored with a two colour optical pyrometer from approximately 3.5 cm above the bed. A complete description of the experimental facility and operation has been reported elsewhere[6].

Five bituminous coals, one subbituminous coal and a lignite were selected for this study. The proximate and ultimate analyses for these fuels are reported in *Table 1*. The Utah, New Mexico and Illinois coals were all classified as high volatile bituminous C (HvCb) coals. The Indiana and Vigrinia coals were similarly classified as hvB and hvA bituminous, respectively. The Montana coal was ranked as a subbituminous B, and the North Dakota fuel was designated as A rank lignite.

All seven coals were compared under similar thermal and stoichiometric conditions. Approximately 4.1 kg of coal, sized at 13 mm through 25 mm, was fired in a 15.3 cm deep fuel bed. The experiments were designed for a nominal superficial burning rate of 1.45 MW/m^2

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(450 000 Btu/h ft^2) at constant bed-region and overall stoichiometric ratios. Overfire air was added at 0.5 m and 1.1 m above the fuel bed in volumetrically equal amounts.

RESULTS AND DISCUSSION

Overall effect of fuel composition

A series of experiments was conducted to assess the overall effect of fuel composition on NO exhaust emissions. Integrated exhaust emissions were compared for the various coals fired under excess air conditions. Integrated exhaust emissions were defined as time averaged emissions measured over a specific control period for each run[4]. Essentially no effect of control interval length on integrated exhaust NO emissions was observed[6]. Complete coal combustion (>95%) was achieved in each run. Bed-region stoichiometric ratios ranged from 1.15 to 1.55, and the average overall stoichiometric ratios remained constant at 1.58 ± 0.07.

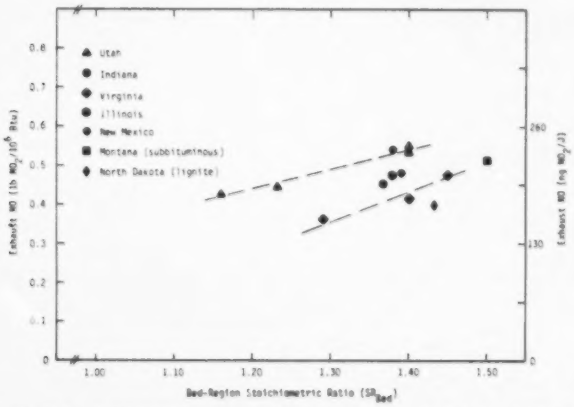

Figure 1 Overall exhaust NO emissions for excess air-firing of coals of varying rank

Figure 1 illustrates the integrated exhaust NO emissions obtained from the seven fuels. The data are reported as NO_x in ng NO_2/J (lb $NO_2/10^6$ Btu) as a function of bed-region stoichiometric ratio. All of the coals showed a strong dependence of NO exhaust emissions on bed-region stoichiometric ratio. This effect has been discussed in previous studies of emissions from mass-burning stokers[1,3–5]. Trends in NO emissions with first stage stoichiometric ratio have been denoted with dashed lines for two bituminous coals. The Utah coal showed the highest emissions under excess air burning. The Virginia coal displayed a slightly greater rate of decrease in NO emissions with decreasing first stage stoichiometric ratio. Both coals were fired at similar burning rates of nominally 1.62 MW/m^2 ± 0.05 MW/m^2 (505 000 Btu/hr ft^2 ± 15 000 Btu/hr ft^2). Overall, the highest NO emissions were produced by the bituminous coals, and the lignite emitted considerably lower levels. No simple correlation relating exhaust NO emissions and coal rank could be determined from the data. Chen and coworkers[7] also noted considerable variability in emissions obtained during the firing of numerous pulverized coals of different rank.

Effect of fuel nitrogen volatility on NO emissions

Inert pyrolysis of the seven coals was conducted to determine volatile and residual char nitrogen fractions. Pyrolysis was conducted isothermally at 1370 K under an argon atmosphere in a high temperature tube furnace. A pyrolysis temperature of 1370 K was selected based on the work of Soloman and Colket[8]. The raw coal samples and pyrolysis char were analysed for carbon, hydrogen and nitrogen with a Perkin–Elmer 240B Elemental Analyser.

Included in *Table 1* is a review of the inert pyrolysis results obtained at 1370 K. The residual char nitrogen is reported as the fraction of original coal nitrogen remaining in the pyrolysis char. The char nitrogen fraction is indicative of the raw coal nitrogen volatility.

Table 1 Fuel analysis

Analysis	UT	IN	VA	IL	NM	MT	ND
Proximate analysis							
Moisture	6.2	6.9	0.9	10.5	6.9	10.9	29.9
Ash	9.6	10.9	13.9	9.4	24.1	4.0	6.8
Volatile matter	37.8	36.7	30.6	38.7	34.5	37.9	29.7
Fixed carbon	46.4	45.5	54.6	41.4	34.5	47.2	33.6
Ultimate analysis							
Moisture	6.2	6.9	0.9	10.5	6.9	10.9	29.9
Carbon	66.4	66.5	71.4	57.8	53.0	57.7	44.7
Hydrogen	4.9	4.8	4.7	4.1	4.5	4.2	2.9
Nitrogen	1.4	1.5	1.5	1.2	1.2	0.5	0.7
Sulphur	0.4	2.2	1.3	4.3	0.6	1.0	0.4
Oxygen	11.1	7.2	6.3	12.7	9.7	21.7	14.7
Ash	9.6	10.9	13.9	9.4	24.1	4.0	6.8
Fuel constituent (%, daf)[a]							
Nitrogen	1.7	1.8	1.8	1.4	1.7	1.7	1.1
Residual char nitrogen (%)							
(Inert pyrolysis at 1370 K)	43.6	35.0	45.4	33.1	50.4	46.8	27.7
Calorific value (as received)							
Kg cal/kg	20 828	21 503	22 660	18 864	16 965	19 660	8 231
Btu/lb	11 571	11 946	12 589	11 946	9 425	10 922	7 573
Calorific value (wet, mmf)[b]							
Kg cal/kg	21 211	24 125	26 303	20 815	22 340	20 488	14 620
Btu/lb	12 895	13 403	14 613	11 564	12 411	11 382	8 122
ASTM rank[c]	hvCb	hvBb	hvAb	hvCb	hvCb	Subbituminous B	Lignite A

[a] daf: dry, ash free
[b] mmf: mineral matter free
[c] hvCb: high volatile C bituminous

The North Dakota lignite appeared to have the highest nitrogen volatility, and the New Mexico bituminous coal showed the highest char nitrogen retention. The data did not indicate a direct correlation between nitrogen volatiles and coal rank. Pohl and Sarofim[9], Blair *et al.*[10], Kobayashi and coworkers[11], and Suuberg and coworkers[12] all demonstrated that during coal devolatilization the fraction of nitrogen retained in the char was most significantly influenced by pyrolysis temperature and to a lesser extent by coal type. However, Solomon and Colket[8] discerned differences between nitrogen volatilities, generally decreasing with increasing coal rank.

Prediction of exhaust NO emissions

A multi-variable linear regression was used to relate integrated exhaust NO emissions to fuel properties. The regression was restricted to emissions obtained under very similar combustion conditions. Exhaust emissions data for the seven fuels fired at a bed-region stoichiometric ratio of 1.40 and an average burning rate of $1.44\,MW/m^2 \pm 0.15\,MW/m^2$ (450000 Btu/h $ft^2 \pm 40000$ Btu/h ft^2) were correlated with inherent fuel nitrogen content and residual char nitrogen fraction based on the work of Chen *et al.*[7] for pulverized coal combustion. They showed that NO emissions were strongly dependent on total nitrogen content, increasing with increasing fuel nitrogen. They further demonstrated that coals which retained significant nitrogen in the char gave NO emissions below the mean emissions measured for 50 coals from throughout the world. These effects were accounted for in their regression correlation. The resulting correlation for this work had the form:

$$NO_{EX} = -70 + 350 \cdot (\text{fuel N}\%) - 109 \cdot (\text{fractional char N retention})$$

and the overall correlation coefficient (r^2) was 0.93, based on seven data sets.

A comparison between the exhaust NO emissions calculated from the regression equation and the experimentally measured emissions is shown in *Figure 2*.

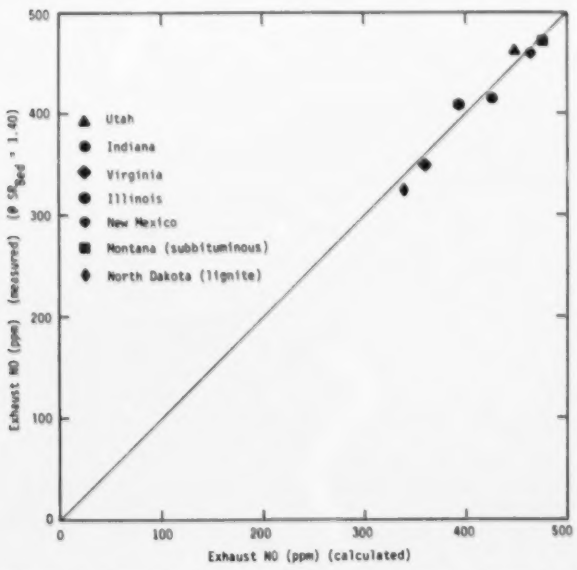

Figure 2 Comparison of measured and calculated exhaust NO emissions from fuel properties

The data show generally good agreement between calculated and measured NO emissions values. The second term indicates that the exhaust emissions increased strongly with increasing fuel nitrogen as expected. Further, the third term has a negative sign because nitrogen retention in the char is beneficial; nitrogen evolved with the hydrocarbon volatiles generally has a higher fractional conversion to NO than that oxidized heterogeneously with the char[13,14]. The intercept value was a numerical result of the narrow range of the data (300 to 500 ppm) and is not considered significant. Thus, the NO emissions could be successfully correlated with fuel nitrogen properties for this specific set of combustion conditions. At other combustion conditions, the numerical constants would undoubtedly change; however, the correlation form appears to be of value in correlating emission results from stoker-fired systems as well as from pulverized coal units.

CONCLUSIONS

Overall exhaust NO emissions were characterized for seven coals of varying rank fired under conditions typical of mass-burning stokers. For all of the coals, decreasing the bed-region stoichiometric ratio resulted in decreased NO emissions. Exhaust emissions showed considerable variability between coal types, even for coals of common rank fired under similar thermal and stoichiometric conditions.

The fuels were characterized by proximate analysis, inherent nitrogen content, and nitrogen volatility. Inert pyrolysis studies indicated that fuel nitrogen volatility was not necessarily related to total nitrogen content. Further, fuel nitrogen conversion was not solely dependent on nitrogen content or volatility. A correlation was developed to estimate NO emissions for several coals based on both the inherent nitrogen content and residual char nitrogen fraction.

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